

First-Principles Momentum Dependent Local Ansatz Approach to the Ground-State Properties of Iron-Group Transition Metals

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The ground-state properties of iron-group transition metals from Sc to Cu have been investigated on the basis of the first-principles momentum dependent local ansatz (MLA) theory. Correlation energy gain is found to show large values for Mn and Fe: 0.090 Ry (Mn) and 0.094 Ry (Fe). The Hund-rule coupling energies are found to be 3000 K (Fe), 1400 K (Co), and 300 K (Ni). It is suggested that these values can resolve the inconsistency in magnetic energy between the density functional theory and the first-principles dynamical coherent potential approximation theory at finite temperatures. Charge fluctuations are shown to be suppressed by the intra-orbital correlations and inter-orbital charge-charge correlations, so that they show nearly constant values from V to Fe: 1.57 (V and Cr), 1.52 (Mn), and 1.44 (Fe), which are roughly twice as large as those obtained by the d band model. The amplitudes of local moments are enhanced by the intra-orbital and inter-orbital spin-spin correlations and show large values for Mn and Fe: 2.87 (Mn) and 2.58 (Fe). These values are in good agreement with the experimental values estimated from the effective Bohr magneton number and the inner core photoemission data.

KEYWORDS: first-principles variational theory, momentum-dependent local ansatz, iron-group transition metals, electron correlations, correlation energy, charge fluctuations, amplitude of local moment

1. Introduction

The iron-group transition metals and compounds are well-known to show a variety of physical properties in cohesion,¹ magnetism,^{2,3} and superconductivity.⁴ To understand their properties, enormous number of band structure calculations have been made over the last several decades. The density functional theory (DFT) has played the central role in these calculations.^{5–7} The DFT with use of the exchange-correlation potentials in the local density approximation (LDA)⁸ or the generalized gradient approximation (GGA)⁹ is known to describe quantitatively the ground-state properties such as the stability of structure,¹⁰ lattice parameter,¹¹ bulk modulus,¹² as well as the magnetization¹¹ and susceptibility¹³ in many transition metals and compounds.

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Although the DFT band theory is successful in many cases in spite of its simplicity, it is also known that the quantitativity of the DFT decreases with increasing Coulomb interaction strength and the range of application is also limited in some cases. In fact, the DFT is based on the Hohenberg-Kohn theorem⁵ which states that the ground-state is given by the functional of electron density. Thus the physical quantities expressed by the two-particle operators as well as excitation spectra cannot be calculated by means of the DFT. Second, the DFT is based on the Kohn-Sham scheme⁶ in which the charge and spin densities are obtained from an independent electron system. Thus the momentum distribution function as well as related mass enhancement factor cannot be described by the DFT when the electron correlations become significant. Furthermore, the LDA and GGA potentials in the DFT do not describe the orbital correlations as well as the Hund-rule correlations in the paramagnetic state,^{2,3} and thus the ground-state energy is overestimated in general in the paramagnetic state.

Because of the reasons mentioned above, the ground-state properties such as the correlation energy, the charge fluctuations, the amplitude of local moment, as well as the momentum distribution function have not yet been fully understood from the quantitative point of view. In order to understand these ground-state properties, we have to take alternative approaches such as the wavefunction method^{14–19} and the dynamical mean field theory (DMFT)^{20,21} or equivalently the dynamical coherent potential approximation (DCPA).^{22–25}

Early calculations of the ground-state properties of iron-group transition metals have been made by Stollhoff and Fulde^{26–28} on the basis of the local ansatz approach (LA) and the d band model. The LA is a Gutzwiller-type variational approach in which the Hilbert space is expanded by the residual Coulomb interactions to describe the local electron correlations.^{29–31} They obtained strong suppression of charge fluctuations by a factor of two as well as strong enhancement of the amplitudes of LM over $3d$ -series elements. Since their calculations are based on the d band model and the LA does not reduce to the correct second order perturbation theory in the weak Coulomb interaction limit, quantitative calculations are desirable to draw a solid conclusion.

Recently we proposed the momentum-dependent local ansatz (MLA) theory in order to describe the ground-state properties quantitatively.^{32–34} The MLA improves the LA by taking into account all the two-particle excited states with momentum-dependent amplitudes. In particular the theory reduces to the Rayleigh-Schrödinger perturbation theory in the weak Coulomb interaction limit as it should be, and describes well the correlated electrons from the weak to strong Coulomb interaction regime. In the next papers,^{35,36} we extended the MLA to the first-principle version using the tight-binding LDA+U Hamiltonian²¹ to describe quantitatively the ground-state properties of the real systems and discussed electron correlation effects in bcc Fe.

Alternative approach to quantitative description of correlated electrons is the first-

principles DMFT (DCPA) combined with the LDA+U Hamiltonian.^{20–25} The LDA+DMFT is a powerful method to strongly correlated electrons and has been applied to many systems. The accuracy of the DMFT however strongly depends on the solver of the impurity problem for correlated electrons. The Quantum Monte-Carlo method (QMC) can describe accurately the finite-temperature properties of the system. But its efficiency is strongly reduced at low temperatures, and the QMC even causes the negative sign problem which prevents us from systematic investigations over wide range of interaction parameters. The exact diagonalization method (ED) is useful to study exactly the physical properties at zero temperature. But it cannot describe the low energy properties associated with the Fermi surface. The numerical renormalization group theory (NRG) describes accurately the low energy excitations, but it does not accurately describe the excitations in high-energy region as well as the energy-integrated quantities. Furthermore it is not applicable to the realistic systems because of the numerical difficulty.

The MLA on the other hand describes quantitatively the quasi-particle weight associated with the low energy excitations as well as the energy-integrated quantities such as the total energy and momentum distribution function without numerical difficulty. In particular, we have shown in the recent paper³⁶ that the first-principles MLA quantitatively explains the mass enhancement factor of bcc Fe obtained by the ARPES experiment, while the LDA+DMFT combined with the three-body theory at zero temperature does not.³⁷ Furthermore the MLA allows us to calculate any static physical quantity because the wavefunction is known. These facts indicate that the first-principles MLA is competitive to the LDA+DMFT at zero temperature and thus it is a suitable approach to correlated electrons.

In the present paper, we investigate quantitatively the systematic change of the ground-state properties of iron-group transition metals from Sc to Cu on the basis of the first-principles MLA. We present the correlation energy, the charge fluctuations, the amplitude of local moment (LM) of the iron-group transition metals in the paramagnetic state. We will clarify the systematic change of these quantities as a function of the conduction electron number and elucidate the interplay among intra-orbital correlations, the inter-orbital charge-charge correlations, and the inter-orbital spin-spin correlations (*i.e.*, the Hund-rule correlations) in the ground-state properties.

In the following section, we outline the first-principles MLA. Starting from the tight-binding LDA+U Hamiltonian and the local ansatz wavefunction with momentum-dependent variational parameters, we obtain the ground-state energy in the single-site approximation (SSA). Using the variational principle, we derive the self-consistent equations for the variational parameters as well as related physical quantities. In §3, we show the numerical results of calculations for the correlation energy, the Hund-rule coupling energy, charge fluctuations, and the amplitude of LM in the paramagnetic state. We discuss the Hund-rule coupling en-

ergy missing in the DFT+LDA band theory and its relation to the Curie temperatures in Fe and Co. We analyze the results with use of the three types of correlations, and demonstrate that the suppression of charge fluctuations are dominated by the intra-orbital correlations and the inter-orbital charge-charge correlations, while the enhancement of amplitude of LM is caused by the intra-orbital correlations and the inter-orbital spin-spin correlations. In the last section, we summarize the results and future problems.

2. First-Principles MLA

We adopt the first-principles LDA+U Hamiltonian with an atom in the unit cell.^{21,25}

$$H = \sum_{iL\sigma} \epsilon_L^0 n_{iL\sigma} + \sum_{iLjL'\sigma} t_{iLjL'} a_{iL\sigma}^\dagger a_{jL'\sigma} + \sum_i \left[\sum_m U_{mm} n_{ilm\uparrow} n_{ilm\downarrow} + \sum_{(m,m')} \left(U_{mm'} - \frac{1}{2} J_{mm'} \right) n_{ilm} n_{ilm'} - 2 \sum_{(m,m')} J_{mm'} \mathbf{s}_{ilm} \cdot \mathbf{s}_{ilm'} \right]. \quad (1)$$

Here ϵ_L^0 is an atomic level of orbital L on site i . $t_{iLjL'}$ is a transfer integral between iL and jL' , $L = (l, m)$ being the s ($l = 0$), p ($l = 1$), and d ($l = 2$) orbitals.^{38,39} $a_{iL\sigma}^\dagger$ ($a_{iL\sigma}$) is the creation (annihilation) operator for an electron on site i with orbital L and spin σ , and $n_{iL\sigma} = a_{iL\sigma}^\dagger a_{iL\sigma}$ is the number operator on the same site i with orbital L and spin σ . The atomic level ϵ_L^0 is calculated from the LDA atomic level ϵ_L by subtracting the d - d Coulomb potential contribution.^{21,23} The third term at the rhs (right-hand-side) of Eq. (1) denotes the on-site Coulomb interactions between d electrons. U_{mm} ($U_{mm'}$) and $J_{mm'}$ are the intra-orbital (inter-orbital) Coulomb and exchange interactions between d electrons, respectively. n_{ilm} (\mathbf{s}_{ilm}) with $l = 2$ is the charge (spin) density operator for d electrons on site i and orbital m . The operator \mathbf{s}_{iL} is defined as $\mathbf{s}_{iL} = \sum_{\gamma\gamma'} a_{iL\gamma}^\dagger (\boldsymbol{\sigma})_{\gamma\gamma'} a_{iL\gamma'}/2$, $\boldsymbol{\sigma}$ being the Pauli spin matrices.

In the first-principles MLA, we split the Hamiltonian H into the Hartree-Fock part H_0 and the residual interaction part H_I :

$$H = H_0 + H_I. \quad (2)$$

The latter is expressed as follows.

$$H_I = \sum_i \left[\sum_L U_{LL}^{(0)} O_{iLL}^{(0)} + \sum_{(L,L')} U_{LL'}^{(1)} O_{iLL'}^{(1)} + \sum_{(L,L')} U_{LL'}^{(2)} O_{iLL'}^{(2)} \right]. \quad (3)$$

The first term is the intra-orbital Coulomb interactions, the second term is the inter-orbital charge-charge interactions, and the third term denotes the inter-orbital spin-spin interactions, respectively. The Coulomb interaction energy parameters $U_{LL'}^{(\alpha)}$ are defined by $U_{LL} \delta_{LL'}$ ($\alpha = 0$), $U_{LL'} - J_{LL'}/2$ ($\alpha = 1$), and $-2J_{LL'}$ ($\alpha = 2$), respectively. The operators $O_{iLL}^{(0)}$, $O_{iLL'}^{(1)}$, and

$O_{iLL'}^{(2)}$ are defined by

$$O_{iLL'}^{(\alpha)} = \begin{cases} \delta n_{ilm\uparrow} \delta n_{ilm\downarrow} \delta_{LL'} & (\alpha = 0) \\ \delta n_{ilm} \delta n_{ilm'} & (\alpha = 1) \\ \delta \mathbf{s}_{ilm} \cdot \delta \mathbf{s}_{ilm'} & (\alpha = 2). \end{cases} \quad (4)$$

Note that δA for an operator A is defined by $\delta A = A - \langle A \rangle_0$, $\langle \sim \rangle_0$ being the average in the Hartree-Fock approximation.

When the Hamiltonian H is applied to the Hartree-Fock wavefunction $|\phi\rangle$, the Hilbert space is expanded by the local operators $\{O_{iLL'}^{(\alpha)}\}$ in the interactions. In order to take into account these states as well as the states produced in the weak Coulomb interaction limit, we introduce the momentum-dependent local correlators $\{\tilde{O}_{iLL'}^{(\alpha)}\}$ ($\alpha = 0, 1$, and 2) as follows.

$$\begin{aligned} \tilde{O}_{iLL'}^{(\alpha)} = & \sum_{\{kn\sigma\}} \langle k'_2 n'_2 | iL \rangle_{\sigma'_2} \langle iL | k_2 n_2 \rangle_{\sigma_2} \langle k'_1 n'_1 | iL' \rangle_{\sigma'_1} \langle iL' | k_1 n_1 \rangle_{\sigma_1} \\ & \times \lambda_{LL'\{2'21'1\}}^{(\alpha)} \delta(a_{k'_2 n'_2 \sigma'_2}^\dagger a_{k_2 n_2 \sigma_2}) \delta(a_{k'_1 n'_1 \sigma'_1}^\dagger a_{k_1 n_1 \sigma_1}). \end{aligned} \quad (5)$$

Here $a_{kn\sigma}^\dagger$ ($a_{kn\sigma}$) is the creation (annihilation) operator for an electron with momentum \mathbf{k} , band index n , and spin σ . These operators are given by those in the site representation as $a_{kn\sigma} = \sum_{iL} a_{iL\sigma} \langle kn | iL \rangle_\sigma$. $\langle kn | iL \rangle_\sigma$ are the overlap integrals between the Hartree-Fock Bloch state ($\mathbf{k}n$) and the local-orbital state (iL).

The momentum-dependent parameters $\lambda_{LL'\{2'21'1\}}^{(\alpha)}$ in Eq. (5) are defined as

$$\lambda_{LL'\{2'21'1\}}^{(0)} = \eta_{L[2'21'1]} \delta_{LL'} \delta_{\sigma'_2\downarrow} \delta_{\sigma_2\downarrow} \delta_{\sigma'_1\uparrow} \delta_{\sigma_1\uparrow}, \quad (6)$$

$$\lambda_{LL'\{2'21'1\}}^{(1)} = \zeta_{LL'[2'21'1]}^{(\sigma_2\sigma_1)} \delta_{\sigma'_2\sigma_2} \delta_{\sigma'_1\sigma_1}, \quad (7)$$

$$\begin{aligned} \lambda_{LL'\{2'21'1\}}^{(2)} = & \sum_{\sigma} \xi_{LL'[2'21'1]}^{(\sigma)} \delta_{\sigma'_2-\sigma} \delta_{\sigma_2\sigma} \delta_{\sigma'_1\sigma} \delta_{\sigma_1-\sigma} \\ & + \frac{1}{2} \sigma_1 \sigma_2 \xi_{LL'[2'21'1]}^{(\sigma_2\sigma_1)} \delta_{\sigma'_2\sigma_2} \delta_{\sigma'_1\sigma_1}. \end{aligned} \quad (8)$$

Here $\{2'21'1\}([2'21'1])$ implies that $\{2'21'1\} = k'_2 n'_2 \sigma'_2 k_2 n_2 \sigma_2 k'_1 n'_1 \sigma'_1 k_1 n_1 \sigma_1$ ($[2'21'1] = k'_2 n'_2 k_2 n_2 k'_1 n'_1 k_1 n_1$). $\eta_{L[2'21'1]}$, $\zeta_{LL'[2'21'1]}^{(\sigma_2\sigma_1)}$, $\xi_{LL'[2'21'1]}^{(\sigma)}$, and $\xi_{LL'[2'21'1]}^{(\sigma_2\sigma_1)}$ are the momentum-dependent variational parameters. It should be noted that $\tilde{O}_{iLL}^{(0)}$, $\tilde{O}_{iLL'}^{(1)}$, and $\tilde{O}_{iLL'}^{(2)}$ reduce to the local correlators, $O_{iLL}^{(0)}$, $O_{iLL'}^{(1)}$, and $O_{iLL'}^{(2)}$, when $\eta_{L[2'21'1]} = \zeta_{LL'[2'21'1]}^{(\sigma_2\sigma_1)} = 1$ and $\xi_{LL'[2'21'1]}^{(\sigma)} = \xi_{LL'[2'21'1]}^{(\sigma_2\sigma_1)} = 1/2$, so that $\{\tilde{O}_{iLL'}^{(\alpha)}\}$ describe the intra-orbital correlations, the inter-orbital charge-charge correlations, and the inter-orbital spin-spin correlations (*i.e.*, the Hund-rule correlations), respectively.

Using the correlators $\{\tilde{O}_{iLL'}^{(\alpha)}\}$ and the Hartree-Fock ground-state wavefunction $|\phi\rangle$, we

construct the first-principles MLA wavefunction as follows.

$$|\Psi_{\text{MLA}}\rangle = \left[\prod_i \left(1 - \sum_L \tilde{O}_{iLL}^{(0)} - \sum_{(L,L')} \tilde{O}_{iLL'}^{(1)} - \sum_{(L,L')} \tilde{O}_{iLL'}^{(2)} \right) \right] |\phi\rangle. \quad (9)$$

The ground-state energy $\langle H \rangle$ is given by

$$\langle H \rangle = \langle H \rangle_0 + N\epsilon_c. \quad (10)$$

Here $\langle H \rangle_0$ denotes the Hartree-Fock energy, N is the number of atoms in the system. ϵ_c is the correlation energy per atom defined by $N\epsilon_c \equiv \langle \tilde{H} \rangle = \langle H \rangle - \langle H \rangle_0$. Note that $\tilde{H} \equiv H - \langle H \rangle_0 = \tilde{H}_0 + H_I$. $\langle \sim \rangle$ ($\langle \sim \rangle_0$) denotes the full (Hartree-Fock) average with respect to $|\Psi_{\text{MLA}}\rangle$ ($|\phi\rangle$). The correlation energy ϵ_c is expressed in the single-site approximation (SSA) as follows.³⁵

$$\epsilon_c = \frac{-\langle \tilde{O}_i^\dagger H_I \rangle_0 - \langle H_I \tilde{O}_i \rangle_0 + \langle \tilde{O}_i^\dagger \tilde{H} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (11)$$

Here $\tilde{O}_i = \sum_\alpha \sum_{\langle L, L' \rangle} \tilde{O}_{iLL'}^{(\alpha)}$. The sum $\sum_{\langle L, L' \rangle}$ is defined by a single sum \sum_L when $L'=L$, and by a pair sum $\sum_{(L, L')}$ when $L' \neq L$. Each element in Eq. (11) has been calculated with use of Wick's theorem.

The variational parameters are determined from the stationary condition $\delta\epsilon_c = 0$ as follows.

$$-\langle (\delta\tilde{O}_i^\dagger) H_I \rangle_0 + \langle (\delta\tilde{O}_i^\dagger) \tilde{H} \tilde{O}_i \rangle_0 - \epsilon_c \langle (\delta\tilde{O}_i^\dagger) \tilde{O}_i \rangle_0 + c.c. = 0. \quad (12)$$

Here $\delta\tilde{O}_i^\dagger$ denotes the variation of \tilde{O}_i^\dagger with respect to $\{\lambda_{LL'\{2'21'1\}}^{(\alpha)}\}$.

Since it is not easy to solve Eq. (12) for arbitrary Coulomb interaction strength, we make use of the following ansatz for the variational parameters, which interpolates between the weak Coulomb interaction limit and the atomic limit.

$$\lambda_{LL'\{2'21'1\}}^{(\alpha)} = \frac{U_{LL'}^{(\alpha)} \sum_\tau C_{\tau\sigma'_2\sigma_2\sigma'_1\sigma_1}^{(\alpha)} \tilde{\lambda}_{\alpha\tau LL'}^{(\sigma_2\sigma_1)}}{\epsilon_{k'_2 n'_2 \sigma'_2} - \epsilon_{k_2 n_2 \sigma_2} - \epsilon_{k'_1 n'_1 \sigma'_1} - \epsilon_{k_1 n_1 \sigma_1} - \epsilon_c}. \quad (13)$$

Here the spin-dependent coefficients $C_{\tau\sigma'_2\sigma_2\sigma'_1\sigma_1}^{(\alpha)}$ are defined by $\delta_{\sigma'_2\downarrow}\delta_{\sigma_2\downarrow}\delta_{\sigma'_1\uparrow}\delta_{\sigma_1\uparrow}$ ($\alpha = 0$), $\delta_{\sigma'_2\sigma_2}\delta_{\sigma'_1\sigma_1}$ ($\alpha = 1$), $-(1/4)\sigma_1\sigma_2\delta_{\sigma'_2\sigma_2}\delta_{\sigma'_1\sigma_1}$ ($\alpha = 2, \tau = l$), and $-(1/2)\sum_\sigma\delta_{\sigma'_2-\sigma}\delta_{\sigma_2\sigma}\delta_{\sigma'_1\sigma}\delta_{\sigma_1-\sigma}$ ($\alpha = 2, \tau = t$), respectively. Note that $l(t)$ implies the longitudinal (transverse) component. The parameters $\tilde{\lambda}_{\alpha\tau LL'}^{(\sigma\sigma')}$ in Eq. (13) are defined by $\tilde{\eta}_{LL'}\delta_{LL'}\delta_{\sigma'-\sigma}$ ($\alpha = 0$), $\tilde{\zeta}_{LL'}^{(\sigma\sigma')}$ ($\alpha = 1$), $\tilde{\xi}_{tLL'}^{(\sigma)}\delta_{\sigma'-\sigma}$ ($\alpha = 2, \tau = t$), and $\tilde{\xi}_{lLL'}^{(\sigma\sigma')}$ ($\alpha = 2, \tau = l$), respectively. The renormalization factors $\tilde{\eta}_{LL'}$, $\tilde{\zeta}_{LL'}^{(\sigma\sigma')}$, $\tilde{\xi}_{lLL'}^{(\sigma)}$, and $\tilde{\xi}_{lLL'}^{(\sigma\sigma')}$ are new variational parameters to be determined. The denominator in Eq. (13) expresses the two-particle excitation energy. $\epsilon_{kn\sigma}$ denotes the Hartree-Fock one electron energy eigenvalue for momentum \mathbf{k} , band index n , and spin σ . Note that when $\tilde{\eta}_{LL'} = \tilde{\zeta}_{LL'}^{(\sigma\sigma')} = 1$ and $\tilde{\xi}_{lLL'}^{(\sigma\sigma')} = \tilde{\xi}_{tLL'}^{(\sigma)} = -1$, the MLA wavefunction (9) reduces to that of the Rayleigh-Schrödinger perturbation theory in the weak Coulomb interaction limit.

Substituting Eq. (13) into the elements in Eq. (12), we obtain the self-consistent equations

for the variational parameters. In the paramagnetic case, the variational parameters $\tilde{\lambda}_{\alpha\tau LL'}^{(\sigma\sigma')}$ are spin independent (, *i.e.*, $\tilde{\lambda}_{\alpha\tau LL'}$), and the self-consistent equations are expressed as follows.³⁵

$$\tilde{\lambda}_{\alpha\tau LL'} = \tilde{Q}_{LL'}^{-1} \left(\kappa_\alpha P_{LL'} - U_{LL'}^{(\alpha)-1} K_{\tau LL'}^{(\alpha)} \right). \quad (14)$$

Here $\tilde{Q}_{LL'}$ has the form $\tilde{Q}_{LL'} = Q_{LL'} - \epsilon_c S_{LL'}$. The constant κ_α is defined by 1 for $\alpha = 0, 1$, and -1 for $\alpha = 2$. The second terms at the rhs of Eq. (14) originates in the matrix element $\langle \tilde{O}_i^\dagger H_I \tilde{O}_i \rangle_0$, *i.e.*, the third term in the numerator of the correlation energy (11). These terms are of higher order in Coulomb interaction and are given by a linear combination of $\{\tilde{\lambda}_{\alpha\tau LL'}\}$. $Q_{LL'}$, $S_{LL'}$, $P_{LL'}$, and $K_{\tau LL'}^{(\alpha)}$ are expressed by means of the Laplace transforms of the Hartree-Fock local densities of states.³⁵

It should be noted that $\tilde{Q}_{LL'}$, $P_{LL'}$, and $K_{\tau LL'}^{(\alpha)}$ contain the correlation energy ϵ_c and the Fermi level ϵ_F . Moreover $K_{\tau LL'}^{(\alpha)}$ are given by the linear combination of $\{\tilde{\lambda}_{\alpha\tau LL'}\}$. The correlation energy ϵ_c is expressed by Eq. (11) with variational parameters (13). The Fermi level ϵ_F is determined by the conduction electron number per atom n_e , which is expressed as

$$n_e = \sum_L \langle n_{iL} \rangle. \quad (15)$$

Taking the same steps as in Eq. (11), we obtain the partial electron number of orbital L on site i in the SSA as follows.

$$\langle n_{iL} \rangle = \langle n_{iL} \rangle_0 + \langle \tilde{n}_{iL} \rangle. \quad (16)$$

Here $\langle n_{iL} \rangle_0$ denotes the Hartree-Fock electron number. The correlation correction $\langle \tilde{n}_{iL} \rangle$ is expressed as follows.

$$\langle \tilde{n}_{iL} \rangle = \frac{\langle \tilde{O}_i^\dagger \tilde{n}_{iL} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (17)$$

Note that $\langle \tilde{O}_i^\dagger \tilde{n}_{iL} \rangle_0$ and $\langle \tilde{n}_{iL} \tilde{O}_i^\dagger \rangle_0$, which correspond to the first and second terms in the numerator of the correlation energy (11), vanish according to Wick's theorem. The other elements at the rhs of Eq. (17) are also calculated by using Wick's theorem. Equations (11), (14), and (15) determine self-consistently the correlation energy ϵ_c , the Fermi level ϵ_F , as well as the variational parameters $\{\tilde{\lambda}_{\alpha\tau LL'}\}$.

The local charge fluctuation and the amplitude of the local moment for d electrons are calculated from the following expressions.

$$\begin{aligned} \langle (\delta n_d)^2 \rangle &= \sum_{L\sigma}^d \langle n_{iL\sigma} \rangle_0 (1 - \langle n_{iL\sigma} \rangle_0) + \sum_{L\sigma}^d \langle \tilde{n}_{iL\sigma} \rangle (1 - 2\langle n_{iL\sigma} \rangle_0) \\ &\quad - \langle \tilde{n}_{id} \rangle^2 + 2 \sum_L^d \langle O_{iLL}^{(0)} \rangle + 2 \sum_{(L,L')}^d \langle O_{iLL'}^{(1)} \rangle, \end{aligned} \quad (18)$$

$$\begin{aligned}
\langle \mathbf{S}^2 \rangle = & \frac{3}{4} \sum_{L\sigma}^d \langle n_{iL\sigma} \rangle_0 (1 - \langle n_{iL\sigma} \rangle_0) + \frac{3}{4} \sum_{L\sigma}^d \langle \tilde{n}_{iL\sigma} \rangle (1 - 2\langle n_{iL-\sigma} \rangle_0) \\
& - \frac{3}{2} \sum_L^d \langle O_{iLL}^{(0)} \rangle + 2 \sum_{(L,L')}^d \langle O_{iLL'}^{(2)} \rangle. \quad (19)
\end{aligned}$$

Here the first terms at the rhs of Eqs. (18) and (19) express the Hartree-Fock contributions. $\langle \tilde{n}_{iL\sigma} \rangle$ in the second terms is given by Eq. (17) in which \tilde{n}_{iL} has been replaced by $\tilde{n}_{iL\sigma}$. $\langle \tilde{n}_{id} \rangle$ in the third term of Eq. (18) is defined by $\sum_L^d \langle \tilde{n}_{iL} \rangle$. Note that \sum_L^d denotes the sum over d orbitals ($l = 2$). The remaining correlation corrections at the rhs of Eqs. (18) and (19) are obtained from the residual interaction elements $\langle O_{iLL'}^{(\alpha)} \rangle$, which are expressed in the SSA as follows.

$$\sum_{\langle L, L' \rangle} \langle O_{iLL'}^{(\alpha)} \rangle = \frac{- \sum_{\langle L, L' \rangle} \langle \tilde{O}_i^\dagger O_{iLL'}^{(\alpha)} \rangle_0 - \sum_{\langle L, L' \rangle} \langle O_{iLL'}^{(\alpha)} \tilde{O}_i \rangle_0 + \sum_{\langle L, L' \rangle} \langle \tilde{O}_i^\dagger O_{iLL'}^{(\alpha)} \tilde{O}_i \rangle_0}{1 + \langle \tilde{O}_i^\dagger \tilde{O}_i \rangle_0}. \quad (20)$$

The elements at the rhs of Eq. (20) are again calculated with use of Wick's theorem.³⁵

3. Numerical Results

In the present calculations, we adopted the same lattice constants and structures as used by Andersen *et al.*³⁹ We constructed the tight-binding (TB) LDA+U Hamiltonians with use of the Barth-Hedin exchange-correlation potentials and the TB linear muffin-tin orbital (LMTO) method within the atomic sphere approximation (ASA). Furthermore we adopted orbital-independent Coulomb and exchange interactions $U_{mm} = U_0$, $U_{mm'} = U_1$ ($m' \neq m$), and $J_{mm'} = J$. These values are obtained from the average Coulomb interaction energies U via the relations $U_0 = U + 8J/5$ and $U_1 = U - 2J/5$, where we used the relation $U_0 = U_1 + 2J$ for the cubic system. We applied the average interactions U obtained by Bandyopadhyay *et al.*⁴⁰ and the average J obtained from the Hartree-Fock atomic calculations.⁴¹ The Coulomb and exchange interaction energies from Sc and Cu are depicted in Fig. 1 as a function of the conduction electron number n_e . The same Hamiltonians and Coulomb-exchange interactions have been applied in the investigations of the excitation spectra in $3d$ transition metals with use of the first-principles dynamical CPA.²³

We performed the self-consistent Hartree-Fock calculations from Sc to Cu in the paramagnetic state using the TB LDA+U Hartree-Fock Hamiltonian H_0 (see Eq. (2)). Figure 2 shows some total densities of states (DOS) obtained by the self-consistent calculations. The d bands sink commonly by $0.02 \sim 0.03$ Ry as compared with those in the LDA bands. The d band widths are broader than the LDA bands for the elements with d electrons less than half, by 30 % for fcc Sc, 15 % for fcc Ti, 10 % for bcc V, and 4 % for bcc Cr, respectively. The widths shrink for the elements with d electrons more than half, by 0 % for fcc Mn, 5 % for bcc Fe, fcc Co and fcc Ni, and 8 % for fcc Cu, respectively, as compared with the LDA

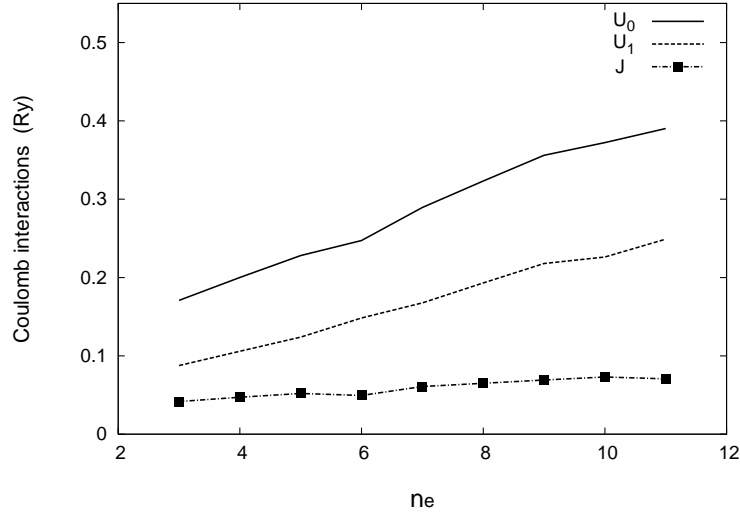


Fig. 1. Intra-atomic Coulomb and exchange energy parameters as a function of the conduction electron number of iron-group transition metals. These parameters are obtained from the band⁴⁰ and atomic⁴¹ calculations. Intra-orbital Coulomb interactions U_0 : solid curve, inter-orbital Coulomb interactions U_1 : dashed curve, exchange interactions J : closed squares and dot-dashed curve.

bands. However the DOS below the Fermi level are basically the same as those in the LDA bands except fcc Cu in which the d bands are shifted by 0.086 Ry towards the lower energy as compared with the LDA.

We solved the self-consistent equations (11), (14), and (15) using the Hartree-Fock energy bands and eigen vectors. Figure 3 shows calculated correlation energies from Sc to Cu. Correlation energy gain $|\epsilon_c|$ increases first with increasing the conduction electron number n_e , shows a large value 0.090 Ry for fcc Mn and the maximum value 0.094 Ry for bcc Fe. Then it rapidly decreases with further increasing n_e . The correlation energy gain is negligible for Cu since the d electron states are almost occupied. Detailed values of correlation energies from Sc to Cu are presented in Table I.

In order to clarify the role of three types of correlations introduced in the MLA wavefunction (9), we calculated the correlation energy due to the intra-orbital correlations $\epsilon_c(\text{intra})$, the correlation energy due to the intra-orbital and inter-orbital charge-charge correlations $\epsilon_c(\text{intra} + \text{cc})$, and the total correlation energy $\epsilon_c(\text{total})$ with the inter-orbital spin-spin correlations (*i.e.*, the Hund-rule correlations). They are defined by ϵ_c when $\tilde{\zeta}_{LL'} = \tilde{\xi}_{LL'} = \tilde{\xi}_{tLL'} = 0$, ϵ_c when $\tilde{\xi}_{tLL'} = \tilde{\xi}_{tLL'} = 0$, and the full ϵ_c , respectively. Note that $|\epsilon_c(\text{intra})|$ is the correlation energy gain due to the reduction of double occupancy on the same orbital. Therefore the energy gain is expected to show the maximum for the half-filled d bands. The shape of the curve is similar to the full ϵ_c as shown in Fig. 3. The contribution of $\epsilon_c(\text{intra})$ to $\epsilon_c(\text{total})$ is about 50 %. The difference between $\epsilon_c(\text{intra} + \text{cc})$ and $\epsilon_c(\text{intra})$ implies the energy gain due

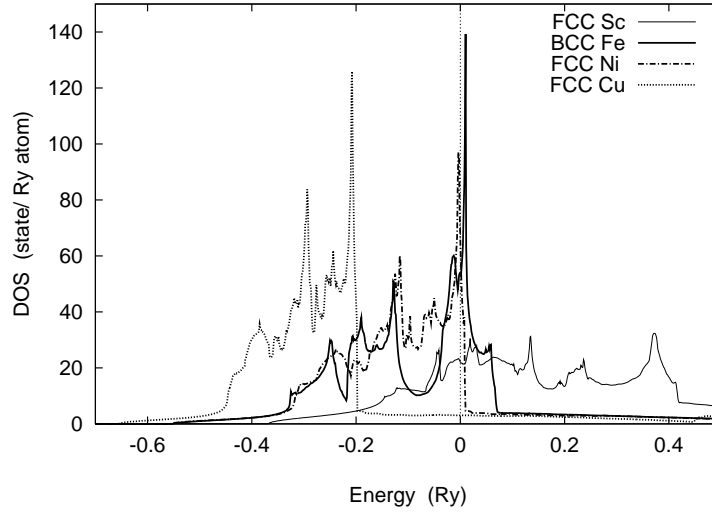


Fig. 2. Calculated densities of states (DOS) for fcc Sc (thin solid curve), paramagnetic bcc Fe (solid curve), paramagnetic fcc Ni (dot-dashed curve), and fcc Cu (dotted curve) in the Hartree-Fock approximation.

to the intra-orbital charge-charge correlations. It is significant in Sc, Ti, and Ni, and makes about 50 % contribution to $\epsilon_c(\text{total})$. In the case of Mn and Fe, its contribution is about 25 %.

The difference between $\epsilon_c(\text{total})$ and $\epsilon_c(\text{intra} + \text{cc})$ indicates the energy gain due to the inter-orbital spin-spin correlations, *i.e.*, the Hund-rule correlations. The Hund-rule correlation energy becomes significant for Mn and Fe and amounts to about 25 % of $\epsilon_c(\text{total})$. The energy is small for fcc Ni, and is negligible for Cu. In Table II, we summarize the Hund-rule coupling energies in iron-group transition metals, which are defined by $\Delta\epsilon_H \equiv \epsilon_c(\text{intra} + \text{cc}) - \epsilon_c(\text{total})$. Mn and Fe show large Hund-rule energies: 0.29 eV (= 0.0216 Ry) and 0.30 eV (= 0.0221 Ry), respectively, which are about 3000 K, indicating that these metals have a well-defined local magnetic moment above the Curie or Néel temperature. In the case of Ni, it is 0.032 eV (= 0.0024 Ry), which is roughly 300 K, indicating that the Hund-rule correlations do not play an important role above the Curie temperature (640 K) in the case of Ni.

The DFT+LDA band theory does not take into account the Hund-rule coupling energy in the paramagnetic state, while the theory does the energy via the polarized exchange-correlation potential in the ferromagnetic state. Thus the magnetic energy E_{mag} defined by the energy difference between the paramagnetic state and the ferromagnetic state is in general overestimated in the DFT+LDA. In fact, the magnetic energy of the bcc Fe (fcc Co) in the DFT+LDA, *i.e.*, $E_{\text{mag}}(\text{LDA})$ is estimated to be about 5000 K⁴² (4000 K⁴³), while the first-principles DCPA yields $E_{\text{mag}}(\text{DCPA}) \sim 2000$ K (2500 K).²⁴ The discrepancies in two approaches are qualitatively explained by taking into account the Hund-rule coupling $\Delta\epsilon_H$

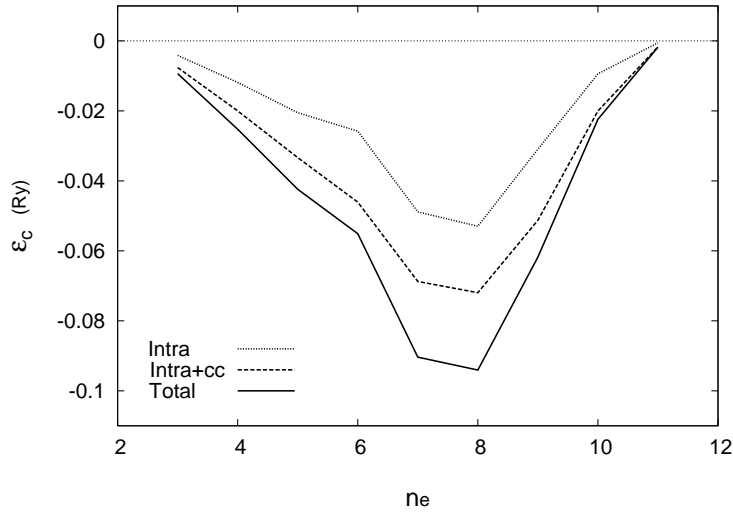


Fig. 3. Systematic change of correlation energy from Sc to Cu as a function of conduction electron number n_e . Dotted curve: correlation energy due to intra-orbital correlations $\epsilon_c(\text{intra})$, dashed curve: correlation energy due to intra-orbital and inter-orbital charge-charge correlations $\epsilon_c(\text{intra} + \text{cc})$, solid curve: total correlation energy including the inter-orbital spin-spin correlations $\epsilon_c(\text{total})$.

Table I. Calculated correlation energies $\epsilon_c(\text{total})$ (Ry) for iron-group transition metals.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
-0.0094	-0.0253	-0.0424	-0.0551	-0.0904	-0.0941	-0.0618	-0.0224	-0.0018

obtained in the present calculation. In fact, if we subtract $\Delta\epsilon_H \sim 3000$ K (1400 K) from $E_{\text{mag}}(\text{LDA}) \sim 5000$ K (4000 K) for bcc Fe (fcc Co), we find $E_{\text{mag}} \sim 2000$ K (2600 K), which is comparable to $E_{\text{mag}}(\text{DCPA}) \sim 2000$ K (2600 K) obtained by the first-principles DCPA.

In the case of Ni, $E_{\text{mag}}(\text{LDA}) \sim 2900$ K,⁴³ while $\Delta\epsilon_H \sim 300$ K. Therefore, the Hund-rule coupling energy does not explain a large difference between $E_{\text{mag}}(\text{LDA})$ and $E_{\text{mag}}(\text{DCPA}) \sim 600$ K.²⁴ The DFT+LDA band theory overestimates the exchange splitting in Ni by a factor of two.^{42,44-46} It is possible that additional error in magnetic energy associated with the overestimate of the exchange splitting explains the discrepancy. Spin-polarized MLA calculations are desired to clarify the origin of the discrepancy in Ni.

Charge fluctuations associated with electron hopping are suppressed by electron correlations. We calculated the local charge fluctuations of d electrons $\langle(\delta n_d)^2\rangle$. As shown in Fig. 4, the charge fluctuations for the Hartree-Fock independent electrons show a parabolic behavior with the maximum 2.44 at $n_e = 7$ (Mn) as a function of the conduction electron number n_e .

Table II. The Hund-rule coupling energies $\Delta\epsilon_H \equiv \epsilon_c(\text{intra} + \text{cc}) - \epsilon_c(\text{total})$ (eV) in iron-group transition metals.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
0.0240	0.0717	0.1229	0.1228	0.2942	0.3008	0.1432	0.0323	0.0012

However the charge fluctuations based on the first-principles MLA are suppressed, and are approximately constant from V to Fe due to electron correlations: 1.57, 1.57, 1.52, and 1.44 for V, Cr, Mn, and Fe, respectively.

Early calculations based on the LA and the d band model with common crystal structure (bcc), and common Coulomb and exchange energy parameters ($U/W_d = 0.5$ and $J/U = 0.2$, W_d being the d band width)²⁸ show $\langle(\delta n_d)^2\rangle = 0.85, 0.70, 0.68$, and 0.87 for the d electron number $n_d = 4$ (V), 5 (Cr), 6 (Mn), and 7 (Fe). These results are considerably smaller than those obtained by the first-principles MLA calculations, and overestimate the atomic character in charge fluctuations by a factor of two. The LA approximation to the charge fluctuations introduces an error typically by about 10 % according to our previous calculations.^{32,33} Although the LA + d -band model calculations mentioned above are not quantitative version, we suggest that the large discrepancy in charge fluctuations between the two theoretical calculations is mainly attributed to the neglect of the hybridization between the sp and d electrons in the model calculations.

We investigated the role of three kinds of electron correlations in the charge fluctuations, taking the same steps as in the correlation energy. As shown in Fig. 4, the intra-orbital correlations make a significant contribution to the suppression of the charge fluctuations (see the difference between $\langle(\delta n_d)^2\rangle(\text{intra})$ and $\langle(\delta n_d)^2\rangle(\text{HF})$). In the case of Mn and Fe, their contributions amount to more than 50 % of the total suppression of the charge fluctuations (*i.e.*, $\langle(\delta n_d)^2\rangle(\text{HF}) - \langle(\delta n_d)^2\rangle(\text{total})$). The inter-orbital charge-charge correlations also make the contributions being comparable to the intra-orbital ones (see the difference between $\langle(\delta n_d)^2\rangle(\text{intra} + \text{cc})$ and $\langle(\delta n_d)^2\rangle(\text{intra})$). The contribution becomes significant when the d electron number deviates from the half filling. On the other hand, the intra-orbital spin-spin correlations (the Hund-rule correlations) hardly make contribution to the charge fluctuations as shown in Fig. 4 (see the difference between $\langle(\delta n_d)^2\rangle(\text{total})$ and $\langle(\delta n_d)^2\rangle(\text{intra} + \text{cc})$).

Figure 5 shows a systematic change of calculated amplitudes of local moment (LM) from Sc to Cu. The amplitude in the Hartree-Fock approximation shows a parabolic behavior with the maximum 1.84 at $n_e = 7$ (Mn). When electron correlations are introduced, the amplitudes are enhanced. The enhancement becomes larger near the half filling of d electrons, and amounts to 50 % for Mn and Fe.

We have examined the role of electron correlations on the amplitude of LM by adding three

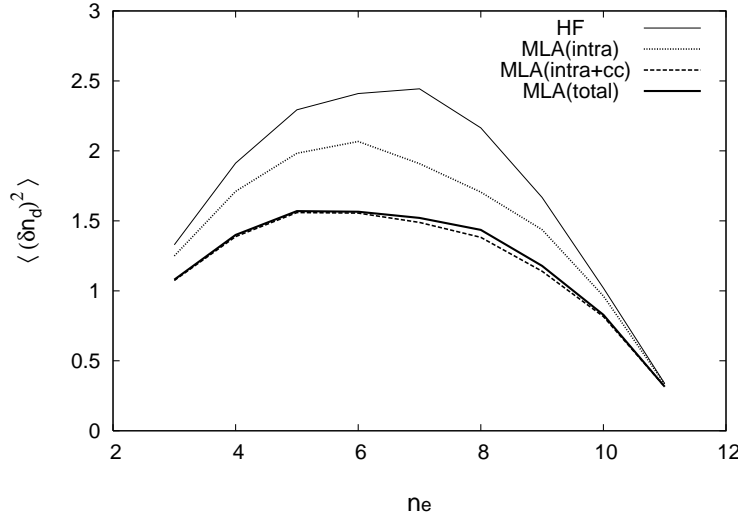


Fig. 4. Systematic change of charge fluctuations $\langle (\delta n_d)^2 \rangle$ from Sc to Cu as a function of conduction electron number n_e . Thin curve: charge fluctuations in the Hartree-Fock approximation $\langle (\delta n_d)^2 \rangle(\text{HF})$, dotted curve: charge fluctuations with intra-orbital correlations $\langle (\delta n_d)^2 \rangle(\text{intra})$, dashed curve: charge fluctuations with intra-orbital and inter-orbital charge-charge correlations $\langle (\delta n_d)^2 \rangle(\text{intra} + \text{cc})$, solid curve: charge fluctuations with full correlations including the inter-orbital spin-spin correlations $\langle (\delta n_d)^2 \rangle(\text{total})$.

kinds of correlations successively. We considered the amplitude with the intra-orbital correlations $\langle \mathbf{S}^2 \rangle(\text{intra})$, the amplitude with both the intra-orbital and inter-orbital charge-charge correlations $\langle \mathbf{S}^2 \rangle(\text{intra} + \text{cc})$, and the amplitude with full correlations $\langle \mathbf{S}^2 \rangle(\text{total})$ as shown in Fig. 5. The intra-orbital correlations significantly enhance the amplitudes because the correlations produce more active spins on each orbital with suppression of the double occupancy. The inter-orbital charge-charge correlations do not make any significant contribution (see the difference between $\langle \mathbf{S}^2 \rangle(\text{intra} + \text{cc})$ and $\langle \mathbf{S}^2 \rangle(\text{intra})$). The inter-orbital spin-spin correlations (*i.e.*, the Hund-rule correlations) make the active spins on different orbitals parallel to each other, thus enhance further the amplitudes as shown in Fig. 5 (see the difference between $\langle \mathbf{S}^2 \rangle(\text{total})$ and $\langle \mathbf{S}^2 \rangle(\text{intra} + \text{cc})$).

We summarize in Table III the calculated amplitudes of LM. We find large amplitudes of LM, $\langle \mathbf{S}^2 \rangle = 2.87$ and 2.58 for fcc Mn and bcc Fe, respectively. In the case of Fe, the experimental value can be estimated from the observed effective Bohr magneton number⁴⁷ $p_{\text{eff}} (= 3.20)$, because the Rhodes-Wohlfarth ratio is equal to 1.0 within 5% error. Using the approximate relation $\langle \mathbf{S}^2 \rangle = p_{\text{eff}}^2/4$, we find the experimental value $\langle \mathbf{S}^2 \rangle = 2.56$, being in good agreement with the present result $\langle \mathbf{S}^2 \rangle = 2.58$.

Alternative way of estimating the amplitude of LM is to use the $3s$ inner core multiplet data in photoemission spectroscopy. The multiplet splitting is expected even in the metallic system

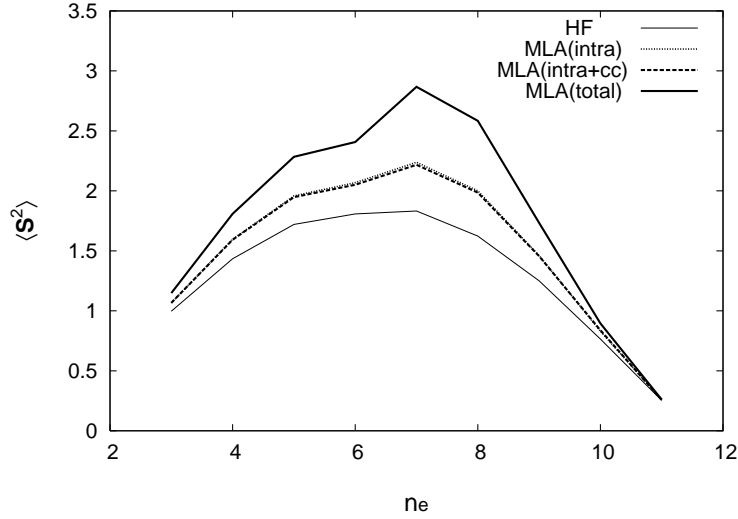


Fig. 5. Systematic change of amplitude of local magnetic moment (LM) $\langle S^2 \rangle$ from Sc to Cu as a function of conduction electron number n_e . Thin curve: amplitude of LM in the Hartree-Fock approximation, dotted curve: amplitude of LM with the intra-orbital correlations $\langle S^2 \rangle(\text{intra})$, dashed curve: amplitude of LM with the intra-orbital and inter-orbital charge-charge correlations $\langle S^2 \rangle(\text{intra} + \text{cc})$, solid curve: amplitude of LM with full correlations including the inter-orbital spin-spin correlations $\langle S^2 \rangle(\text{total})$.

Table III. Calculated amplitudes of local moments $\langle S^2 \rangle$ in iron-group transition metals.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
1.148	1.809	2.284	2.407	2.868	2.583	1.733	0.895	0.260

when the d -electron charge fluctuations are significantly suppressed.⁴⁸ Using the experimental data of the 3s core spectra and the localized model, the amplitudes of LM are estimated to be $\langle S^2 \rangle = 2.8$ for α -Mn⁴⁹ and $\langle S^2 \rangle = 2.5$ for bcc Fe.⁵⁰ These values are again in good agreement with the present results 2.87 for fcc Mn and 2.58 for bcc Fe.

The amplitudes of LM calculated by the LA and the d band model are reported to be 4.0 for Mn and 2.9 for Fe.²⁸ These values are considerably overestimated as compared with the present results: 2.87 for Mn and 2.58 for Fe. We suggest that the overestimate of the amplitudes is mainly due to the neglect of the hybridization between the sp and d electrons in the LA + d band model.

4. Summary

We have investigated the quantitative aspects of the ground-state properties of iron-group transition metals from Sc to Cu on the basis of the first-principles momentum dependent local

ansatz approach (MLA) which we recently developed. The theory reduces to the Rayleigh-Schrödinger perturbation theory in the weak Coulomb interaction limit, and describes quantitatively the ground-state of correlated electrons by means of the self-consistent momentum-dependent variational parameters for the two-particle excited states.

We obtained the correlation energy, the local charge fluctuations, and the amplitudes of local moments (LM) in the paramagnetic state, and clarified the role of three types of electron correlations in these quantities: the intra-orbital correlations, the inter-orbital charge-charge correlations, and the inter-orbital spin-spin correlations (, *i.e.*, the Hund-rule correlations).

Calculated correlation energy gain curve shows a peak near the half-filled d electron number. We obtained large correlation energy gains 0.090 Ry for fcc Mn and 0.094 Ry for bcc Fe. We found that both the intra-orbital and the inter-orbital correlations make significant contribution to the correlation energies for Mn and Fe. The inter-orbital charge-charge correlations become significant when the d electron number deviates from the half-filling.

We calculated the Hund-rule coupling energies $\Delta\epsilon_H$ which are not taken into account in the paramagnetic calculations of the DFT+LDA band theory. We found that the energy $\Delta\epsilon_H$ shows a large value for Mn, Fe, and Co: 0.29 eV (Mn), 0.30 eV (Fe), 0.14 eV (Co), while it is not essential for the magnetism of Ni: 0.03 eV (Ni). We pointed out that the Hund-rule coupling energy can resolve a large difference in magnetic energy E_{mag} between the DFT+LDA and the first-principles DCPA. The magnetic energy in the DFT+LDA, *i.e.*, $E_{\text{mag}}(\text{LDA})$ is overestimated because of the lack of the Hund-rule coupling energy $\Delta\epsilon_H$ in the paramagnetic state. Subtracting $\Delta\epsilon_H$ from $E_{\text{mag}}(\text{LDA})$, we obtained $E_{\text{mag}} \sim 2000$ K for bcc Fe and 2600 K for fcc Co, being comparable to those obtained by the first-principles DCPA.

The intra-orbital correlations suppress the double occupancy on the same orbital to reduce the Coulomb energy on each orbital, so that the correlations suppress the d electron hopping and thus charge fluctuations. The inter-orbital charge-charge correlations suppress the creation of electron pairs on the different d orbitals. The correlations therefore also suppress the d electron hopping and lead to the suppression of charge fluctuations for d electrons. We found that Mn shows the strongest suppression of charge fluctuations. The deviation from the Hartree-Fock charge fluctuations is found to be 0.92 in the case of fcc Mn. Calculated charge fluctuations are nearly constant from V to Fe due to electron correlations: 1.57 (V), 1.57 (Cr), 1.52 (Mn), 1.44 (Fe). These values are roughly twice as large as those obtained by the early calculations based on the LA + d band model.

The intra-orbital correlations also increase the active spins on each d orbital as the result of suppression of the double occupancy on the d orbitals. The inter-orbital spin-spin correlations, *i.e.*, the Hund-rule correlations make these spins on different d orbitals parallel, and lead to the enhancement of the amplitudes of LM. The enhancement effects become maximum near the half-filling of d electrons. We found that the enhancement amounts to 50 % for Mn and

Fe, so that we obtained $\langle S^2 \rangle = 2.87$ (Mn) and 2.58 (Fe). These results are in good agreement with the experimental values, 2.8 (α -Mn) estimated from the inner core photoemission data and 2.56 estimated from the effective Bohr magneton number. Early calculations based on the LA + d band model overestimate the amplitudes of LM.

In order to make these conclusions clearer, it is desirable to investigate the ground-state properties of the ferromagnetic Fe, Co, and Ni with use of the first-principles spin-polarized MLA.

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